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(54) Title: A METHOD FOR PREPARING ORGANIC FLUOROCOMPOUNDS

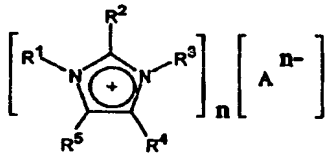
(57) Abstract: The present invention relates to a method for preparing organic fluorocompounds, more particluraly to a method for preparing organic fluorocompounds by means of reaction of alkyl halide or alkyl sulfonate with fluoro salt in the presence of imidazolium salt as a solvent or mixture solvent of imidazolium salt and oragnic solvent. Such a method reduces the reaction time and improves the yield considerably by being accomplished under a mild reaction condition, such that the organic fluorocompounds can be prepared in an economic manner.

A METHOD FOR PREPARING ORGANIC FLUOROCOMPOUNDS

TECHNICAL FIELD

The present invention relates to a method for preparing organic fluorocompounds, more particularly a method for preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salts in the presence of a solvent, wherein the solvent is imidazolium salt represented by the following formula 1 or a mixture solvent thereof.

FORMULA 1



wherein, R^1, R^2, R^3, R^4, R^5 and n are defined in the description

BACKGROUND OF THE INVENTION

Fluorine atoms are almost the same size as that of hydrogen atoms. They show strong polarity and have hydrophobic properties. Organic fluorocompounds comprising such fluorine atoms have specific chemical and physiological properties which differ from those of ordinary organic compounds, and thus they can be usefully

used as medicine, agricultural chemicals, dyes, and high molecules [Gerstenberger, M. R. C., Haas, A. *Angew. Chem.*, Int. Ed. Engl. 1981, 20, 647; Filler, R. In Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications, Filler, R., Ed., Studies in Organic Chemistry 48, Elservier, New York, 1993, p 1-23].

In general, organic fluorocompounds are prepared by means of the substitution reaction, reacting alkyl halide or alkyl sulfonate with fluoride salts as represented by chemical reaction 1.

CHEMICAL REACTION 1

$$R{-}X + MF_n \xrightarrow[\text{solvent}]{} R{-}F$$

wherein, halide is not F, and is selected from a group consisting of Cl, Br and I, and sulfonate is $-SO_3R^{12}$, wherein, R^{12} is alkyl or aryl group, more particularly, the alkyl is preferably $C_1 \sim C_{12}$ alkyl or halo $C_1 \sim C_{12}$ alkyl group. Preferable examples of alkyl sulfonate comprising the alkyl group is selected from a group consisting of methansulfonate, ethansulfonate, isopropansulfonate, chloromethansulfonate, trifluoromethansulfonate and chloroethansulfonate. Also, the aryl group is preferably phenyl, $C_1 \sim C_4$ alkyl phenyl, halo phenyl, $C_1 \sim C_4$ alkoxy phenyl or nitrophenyl group. Preferable examples of aryl

sulfonate comprising the aryl group is selected from a group consisting of methylphenylsulfonate, ethylphenylsulfonate, chlorophenylsulfonate, bromophenylsulfonate, methoxyphenylsulfonate and nitrophenylsulfonate.

At this time, fluoride salts (MF_n), as a supply source of fluoride ion, use alkali metal fluorides comprising alkali metal selected form a group consisting of lithium, sodium, potassium, rubidium and cesium; alkali earth fluorides comprising alkali earth metal selected from a group consisting of magnesium, calcium, strontium and barium; or ammonium fluorides comprising ammonium selected from a group consisting of ammonium and tetraalkylammonium.

In particular, among the various fluoride salts exhibited above, potassium fluoride (KF) is commonly used as a supply source of fluoride ion due to its moderate price and its stability.

At this time, n is an integer of 1~2.

In the method for preparing organic fluorocompounds, it is disclosed that alkyl fluoride is prepared by reacting alkyl halide with potassium fluoride in the presence of an ethylene glycol solvent [Hoffmann, F. W. J. Am. Chem. Soc., 1948, 70, 2596.].

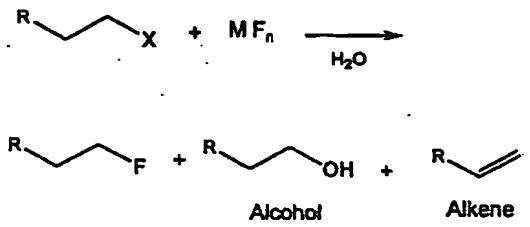
But, despite the advantages of potassium fluoride, the above preparation method has a disadvantage that the reactivity level drops due to the low solubility of potassium fluoride, and thus organic fluorocompounds should be prepared at a temperature above 140℃ for a long period of time, and the yield is low.

To improve the solubility of potassium fluoride and increase the reactivity of fluoride ion, it is disclosed that the reaction is accomplished in the presence of 18-crown-6 ether, which is capable of forming a strong bond with metal ion, as a catalyst under a relatively low temperature of 80~90℃ and a mild condition to prepare organic fluorocompounds of high yield [Liotta, C. L., Harris, H. P. J. Am. Chem. Soc., 1974, 96, 2250.].

But, this preparation method has disadvantages that 18-crown-6 ether is expensive and that the reaction time is long. Further, during the preparation, fluoride ion activates as a base, and thus mass produces alkene, a side product.

In general, it is known that the preparation method of organic fluorocompounds using fluoride salt accompanies a side reaction as the following chemical scheme 2.

CHEMICAL SCHEME 2



For example, if tetrabutylammonium fluoride is used as a fluoride salt, an organic fluorocompound of an excellent yield is prepared at a mild reaction condition [Cox, D.P., Terpinski, J., Lawrynowicz, W. J. Org. Chem. 1984, 49, 3216.]. However, the above tetrabutylammonium fluoride accompanies a problem that a great quantity of alcohol, a side product of water is obtained always in the presence of water.

Therefore, when preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salts, a preparation method which can reduce the reaction time by enhancing the activity of fluoride salt and can reduce the amount of side products such as alkene and alcohol that is obtained by eliminating or minimizing the influence on water is required.

In general, compounds which are stable in air and water with no volatility or inflammability, which exist as liquid at a temperature below 100°C are classified as Ionic

Liquid.

An example of such ionic liquid is imidazolium salt which is represented by formula 1 of the present invention. Imidazolium salt has the properties of usual ionic liquids. That is, it has a superior melting capacity against various organic matters and inorganic matters, it is not dissolved in water, and it is stable in various chemical reaction conditions. Especially, imidazolium salt shows an outstanding solvent effect due to its strong ionic character, which cannot be observed in ordinary organic solvents.

Moreover, since it does not have volatility at all, it can be recollected after the reaction with no loss, and thus, is being attracted as a clarifying solvent of the next generation [T. Welton, Chem. Rev., 1999, 99, 2071; P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed., 2000, 39, 3772; C. E. Song, W. H. Shim, E. J. Roh, S.-g. Lee, J. H. Choi, Chem. Commun., 2001, 1122; C. E. Song, W. H. Shim, E. J. Roh, J. H. Choi, Chem. Commun., 2000, 1695].

DISCLOSURE OF THE INVENTION

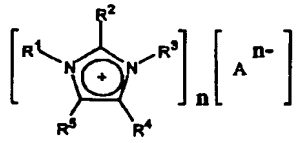
Hereupon, the present inventors made an effort to solve the above problems and thus, prepared organic fluorocompounds by reacting alkyl halide or alkyl sulfonate

with fluoride salt in the presence of solvent, wherein the solvent is imidazolium salt or a mixture solvent of imidazolium salt and organic solvent. Further, the present invention has been completed by finding out that organic compounds with an outstandingly enhanced yield can be obtained under a mild reaction condition.

It is an object of the present invention to provide a method for preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salts in the presence of a solvent, wherein the solvent is imidazolium salt or a mixture solvent of imidazolium salt and organic solvent.

In order to accomplish the aforementioned object, the present invention provides a method for preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salts in the presence of a solvent, wherein the solvent is imidazolium salt represented by formula 1 or a mixture solvent of imidazolium salt and organic solvent.

FORMULA 1



wherein, R^1 is $C_1 \sim C_{18}$ alkyl group; R^2, R^3, R^4 and R^5

are hydrogen or C_1~C_{18} alkyl group;

n is an integer of 1~3,

A is an anion capable of forming salts.

The present invention provides a method for preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salt in the presence of a solvent, wherein the solvent is imidazolium salt represented by formula 1 or a mixture solvent of imidazolium salt and organic solvent. The reaction is accomplished at 20~150℃ for 30 minutes~24 hours, preferably at 70~120℃ for 1~10 hours, more preferably at 60~110℃ for 1.5~4 hours.

The imidazolium salts, represented by formula 1, can increase the melting point, affinity with water and chemical stability according to the composition of cation group and anion group of the macromolecule.

The melting point is higher as the number of carbon in the alkyl group increases and as the number of alkyl substituent increases. In order to raise the melting point, the reaction temperature should be raised. Taking this into consideration, R^1 is C_1~C_{18} alkyl group, preferably C_1~C_8 alkyl group, more preferably C_1~C_4 alkyl group. The C_1~C_4 alkyl group includes methyl, ethyl, propyl, butyl, isopropyl, t-butyl, etc.

R^2 is hydrogen or $C_1 \sim C_{18}$ alkyl group, preferably hydrogen or $C_1 \sim C_6$ alkyl group, more preferably hydrogen or methyl group.

R^3 is hydrogen or $C_1 \sim C_{18}$ alkyl group, preferably hydrogen or $C_1 \sim C_8$ alkyl group, more preferably $C_2 \sim C_8$ alkyl group. The $C_2 \sim C_8$ alkyl group includes ethyl, propyl, butyl, pentyl, hextyl, heptyl, octyl etc.

R^4 and R^5 are hydrogen or $C_1 \sim C_{18}$ alkyl group, preferably hydrogen or $C_1 \sim C_6$ alkyl group, more preferably hydrogen.

Particular examples of imidazolium salt include salts of 1-ethyl-3-methyl-imidazolium(emeim), 1-methyl-3-propyl-imidazolium(pmim), 1-buthyl-3-methyl-imidazolium(bmim), 1-methyl-3-pentyl-imidazolium(mpim), 1-hecyl-3-methyl-imidazolium(hmim), 1-heptyl-3-methyl-imidazolium(hpmim), 2,3-dimethyl-1-propyl-imidazolium and 1-propyl-2,3,4,5-tetramethyl-imidazolium; preferably, salt of 1-buthyl-3-methyl-imidazolium.

The melting point, affinity with water and chemical stability of imidazolium salt varies according to substituents and anion.

The anion of imidazolium salt should affect the physical and chemical properties of imidazolium salt and

its chemical stability, but should not cause any side reactions and should not be analyzed. Any anion capable of forming salts can be used.

Preferably, anion A is MF_k^-, R^6O^-, $R^7R^8N^-$ or $R^9R^{10}R^{11}C^-$, wherein M is an element of 3~15 class in periodic table of elements(IUPAC version); k is an integer of 2~6; R^6 is C_1~C_{12} halosufone, halo C_1~C_{12} alkylsulfone, C_1~C_4 alkyl arylsulfone, halo arylsulfone, halosulfone, phosphoryl or perfluoro C_1~C_{12} alkylcarbonyl group; R^7, R^8, R^9, R^{10} and R^{11} are independent from each other and can be C_1~C_{12} alkylsulfone, halo C_1~C_{12} alkylsulfone, C_1~C_4 alkyl arylsulfone, halo arylsulfone.

Particular examples of the anion include tetrafluoroborate(BF_4), hexafluorophosphate(PF_6), hexafluoroantimonate(SbF_6), trifluoromethansulfonate(OSO_2CF_3, OTf) and bis(trifluorosulfonyl)imide($N(SO_2CF_3)_2$, NTf_2).

The imidazolium salt of the present invention increases the solubility of fluoride salt, increases the displacement reaction rate of fluoride ion, and inhibits the side reaction caused by water, by being used as a single solvent or a mixture solvent which is mixed with an organic solvent.

As for organic solvents, any solvent which is chemically stable in fluoride reaction can be used as a

mixture solvent. More particularly, organic solvents can be selected from a group consisting of acetonitrile, tetrahydrofuran, 1,4-dioxane and t-butanol, preferably acetonitrile.

When used as a single solvent or as a mixture solvent mixed with an organic solvent, the content of imidazolium salt used in the present invention is 0.2~5.0 equivalents against alkyl halide or alkyl sulfonate, preferably 0.5~3.0 equivalents.

The fluoride salts, which provide fluoride ion when organic fluorocompounds are prepared, can use alkali metal fluorides consisting of alkali metal selected from a group consisting of lithium, sodium, potassium, rubidium and cesium; alkali earth metal fluorides consisting of alkali earth metal selected from a group consisting of magnesium, calcium, strontium and barium; or ammonium fluoride.

The ammonium fluoride is selected from a group consisting of forth ammonium fluorides such as tetrabutylammonium fluoride, benzyltrimethyl ammonium fluoride, etc.; third ammonium fluoride such as triethylammonium fluoride, tributylammonium fluoride, etc.; secondary ammonium fluoride such as dibutylammonium fluoride, dihexylammonium fluoride, etc.; first ammonium

fluoride such as butylammoium fluoride, hexylammonium fluoride, etc., preferably potassium fluoride.

The potassium fluoride can be used as a form absorbed on supporters of various forms, for example, as a form absorbed on supporters such as celite, molecular seive, alumina, silicagel, etc.

At this time, the content of fluoride salts is 1.0~10.0 equivalents, preferably 3.0~6.0 equivalents against alkyl sulfonate.

Meanwhile, if alkyl halide or alkyl sulfonate is reacted with fluoride salts having an isotope, an organic fluorocompound having an isotope can be prepared.

At this time, a substitution reaction is performed by reacting the fluoride ion of fluoride salt having an isotope with the anion of imidazolium salt, wherein the anion of imidazolium salt is an anion that can smoothly substitute fluoride ion. Preferably, the anion of the imidazolium salt is selected from a group consisting of R^6O^-, $R^7R^8N^-$ or $R^9R^{10}R^{11}C^-$ form than MF_k^- form, wherein, R^6 is C_1~C_{12} alkylsulfone, halo C_1~C_{12} alkylsulfone, C_1~C_4 alkyl arylsulfone, halo arylsulfone, halosulfone, phosphoryl or perfluoro C_1~C_{12} alkylcarbonyl group; R^7, R^8, R^9, R^{10} and R^{11} are all independent and can be C_1~C_{12} alkylsulfone, halo C_1

~C_{12} alkylsulfone, C_1~C_4 alkyl arylsulfone, and halo arylsulfone. Preferable examples of the anion include trifluoromethansulfonate(OSO_2CF_3, OTf) and bis(trifluorosulfonyl)imide($N(SO_2CF_3)_2$, NTf_2).

In a method for preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salts in the presence of solvent, wherein the solvent is imidazolium salt or a mixture solvent of imidazolium salt and organic solvent, the yield of the main product, organic fluorocompounds can selectively be kept above 85% by inhibiting the creation of side reaction.

On the other hand, in accordance with the examples of the present invention, when 18-crown-6 ether, commonly used in prior preparation methods of organic fluorocompound, was used, the yield was low due to the low solubility of fluoride salt. Further, when the imidazolium salt of the present invention was not added during the reaction, organic fluorocompounds were not obtained at all (Table 1).

Therefore, the strong ionic character of the imidazolium salt of the present invention enhances its melting capacity against organic matters and inorganic matters, enables it to overcome the disadvantages of the prior art, whereas the low solubility of fluoride salt

reduces its activity. Further, by enhancing the solubility of fluoride salt, the reaction time can be reduced and the yield can be raised by increasing the activity and reaction rate of fluoride salt.

Also, due to its superior melting capacity against organic matters and inorganic matters, and its insolubility against water, imidazolium salt inhibits side product from being obtained from the effect of water. Therefore, less side products such as alcohol and alkene can be obtained.

A better understanding of the present invention may be obtained in light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention.

EXAMPLES

<Example 1> Preparation of organic fluorocompound 1

2-(3-methansulfonyloxypropoxy)naphthalene(280 mg, 1.0 mmol) and potassium fluoride(290 mg, 5.0 mmol) were dissolved in 5.0 ml of [bmim][BF_4] to prepare a reaction solution. The reaction solution was stirred at 100°C for 2 hours. The solution was extracted with 7 ml of ethyl acetate for 3 times and the extracted solution was dried with anhydrous sodium sulfonate, filtered and concentrated using a vacuum distillation apparatus. The concentrated solution was purified with column

chromatography(ethylacetate:n-hexane=1:20) to obtain 2-3-fluoropropoxy)naphthalene (174 ㎎, 85%).

<Examples 2~11> Preparation of organic fluorocompounds 2~11

Except that a mixture solvent comprising [bmim][BF_4] was used and the reaction time was changed as shown in the following table 1, the reaction was performed in the same manner as described in Example 1.

The organic fluorocompounds were prepared in the condition as shown in the following table 1, and the following chemical scheme 3 represents 2-(3-fluoropropxy)naphtalene(A), 2-(3-hydroxypropoxy)naphtalene(B) and 2-(aryloxy)naphtalene(C), which are obtained while preparing the organic fluorocompounds.

<COMPARATIVE EXAMPLE 1> Preparation of organic fluorocompound 1

2-(3-methansulfonyloxypropoxy)naphthalene(280 ㎎, 1.0 mmol) and potassium fluoride(290 ㎎, 5.0 mmol) were dissolved in 5 ㎖ of acetontrile, without adding 5.0 ㎖ of [bmim][BF4], to prepare a reaction solution. The reaction solution was stirred for 24 hours at 100℃.

As a result, the reaction was not accomplished, and

thus, it has been certified that it is essential to use [bmim][BF_4] as a single solvent or a mixture solvent in order to prepare organic fluorocompounds.

<COMPARATIVE EXAMPLE 2> Preparation of organic fluorocompound 2

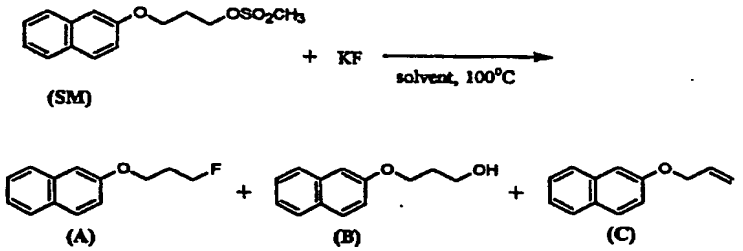
2-(3-methansulfonyloxypropoxy)naphthalene(280 mg, 1.0 mmol) and potassium fluoride(290 mg, 5.0 mmol) were dissolved in a mixture solvent of 18-crown-6(529 mg, 2.0 mmol) and 3.2 ml of acetonitrile, instead of [bmim][BF_4], to prepare a reaction solution. The reaction solution was stirred for 24 hours at 100℃. The stirred solution was extracted with 7 ml of ethyl acetate for three times. The extracted solution was dried with anhydrous sodium sulfate, filtered and concentrated using vacuum distillation apparatus. The concentrated solution was purified with column chromatography(ethylacetate:n-hexane=1:20) to obtain 2-(3-fluoropropoxy)naphthalene(82 mg, 40%).

TABLE 1

	Solvent composite			Reaction time	Yield			
	[bmim][BF_4] ml(eq)	CH_3CN ml	H_2O μl(eq)		SM	A	B	C
Ex.1	5.0	-	-	2.0	-	85	-	10
Ex.2	5.0	-	90(5)	1.5	-	92	-	-
Ex.3	3.2	1.6	90	1.5	-	93	Trace	-
Ex.4	3.0	1.5	-	1.5	-	86	-	11
Ex.5	3.0	1.5	500	1.5	-	88	6	-
Ex.6	2.5	2.5	90	1.5	-	93	Trace	-
Ex.7	1.6	3.2	90	1.5	-	94	-	-
Ex.8	1.0	4.0	90	1.5	-	92	-	-

Ex.9	0.57(3)	4.4	90	3.0	--	91	Trace	-
Ex.10	0.19(1)	4.8	90	6.0	-	89	Trace	-
Ex.11	0.1(0.5)	5.0	90	12	Trace	84	8	trace
Com. Ex.1	-	5.0	0	24	86	Trace	-	-
Com. Ex.2	18-crown-6(2)	5.0	0	24	53	40	-	-

CHEMICAL SCHEME 3



As shown in table 1, when [bmim][BF_4], which is used as an imidazolium salt of the present invention, is used as a single solvent or a mixture solvent wherein acetonitrile is mixed with water, 2-(3-fluoropropoxy)naphtalene(A) was obtained as an organic fluorocompound having a yield of above 85%.

Also, when [bmim][BF_4] 0.5 ~ 3.0 equivalents are used as a mixture solvent mixed with an organic solvent, even though the reaction time gets a little longer, the main product was obtained in a good yield of above 85% (Example 9~Example 11).

On the other hand, as in comparative example 1, wherein the reaction is performed without adding

[bmim][BF_4], or when 18-crown-6 ether is used as in the preparation methods of prior organic fluorocompounds, the reaction has been performed for 24 hours. As a result, it has been found out that the reaction has not been accomplished at all or was performed in a yield of 40%, which proves that [bmim][BF_4] is essential in preparing organic fluorocompounds.

Further, as a result from using [bmim][BF_4] as a mixture solvent mixed with an organic solvent or water, as shown in example 2, when being mixed with 5 equivalents of water, the yield of the main product, 2-(3-fluoropropoxy)naphtalene(A) has increased to 92%. However, as for example 5, when being mixed with a large quantity of water, it has been found out that a side product, alcohol was obtained.

<EXAMPLE 12> Preparation organic fluorocompound 12

2-(3-methansulfonyloxypropoxy)naphthalene(280 ㎎, 1.0 mmol) and potassium fluoride(290 ㎎, 5.0 mmol) were dissolved in a mixture solvent of [bmim][PF6] 1.5 ㎖, acetonitrile 3.0 ㎖ and H_2O(90 ㎕, 5.0 mmol) to prepare a reaction solution. The reaction solution was stirred for 2 hours at 100℃. The stirred solution was extracted with 7 ㎖ of ethylacetate for three times. The extracted solution was dried with sodium sulfate, filtered and concentrated

using vacuum distillation apparatus. The concentrated solution was purified with column chromatography(ethylacetate:n-hexane=1:20) to obtain 2-(3-fluoropropoxy)naphthalene(184 mg, 90%).

<EXAMPLES 13~17> Preparation of organic fluorocompounds 13~17

Except that the imidazolium salts, the organic solvents being used and the reaction time were changed as shown in the following table 2, the reaction was performed in the same manner as described in Example 12.

TABLE 2

	Imidazolium salt	Organic solvent	Reaction time(H)	yield			
				SM	A	B	C
Ex.12	[bmim][PF_6]	CH_3CN	2.0	-	90	trace	-
Ex.13	[bmim][SbF_6]	CH_3CN	2.0	-	93	-	-
Ex.14	[bmim][Otf]	CH_3CN	3.0	-	52	8	6
Ex.15	[bmim][NTf_2]	CH_3CN	3.0	32	20	trace	5
Ex.16	[bmim][BF_4]	1,4-dioxane	1.5	-	91	-	-
Ex.17	[bmim][BF_4]	t-BuOH	1.5	-	85	trace	-

As shown in table 2, if the anion of imidazolium salt was OTf^- or NTf_2^-, 2-(3-fluoropropoxy)naphtalene as a main product(A) was obtained at a low yield, but if the anion of imidazolium salt was BF_4^-, PF_6^- or SbF_6^-, organic fluorocompounds were obtained having a yield of above 90%.

Also, if the solvent was a mixture solvent of imidazolium and organic solvent such as tetrahydrofuran, 1,4-dioxane or t-butanol as well as acetonitrilewith

imidazolium salt, organic fluorocompounds were obtained having a yield of above 85%.

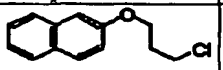
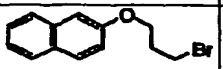
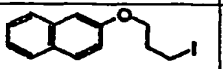
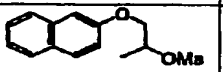
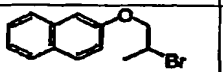
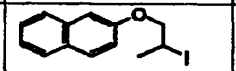
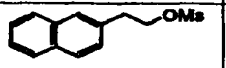
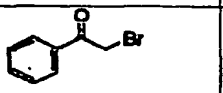
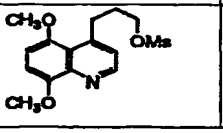
<EXAMPLE 18> Preparation of organic fluorocompound 18

2-(3-chloropropoxy)naphthalene(221 mg, 1.0 mmol) and potassium fluoride(290 mg, 5.0 mmol) were dissolved in a mixture solvent of [bmim][BF4] 1.5 ml, acetonitrile 3.2 ml and H_2O(90 μl, 5.0 mmol) to prepare a reaction solution. The reaction solution was stirred for 24 hours at 110℃. The stirred reaction solution was extracted with 7 ml of ethylacetate for three times. The extracted solution was dried with sodium sulfonate, filtered and concentrated using vacuum distillation apparatus. The concentrated solution was purified with column chromatography(ethylacetate:n-hexane=1:20) to obtain 2-(3-fluoropropoxy)naphthalene(135 mg, 66%).

<EXAMPLES 19~27> Preparation of organic fluorocompounds 19~27

Except that 1.0 mmol of various alkyl halide or alkyl sulfonate, shown in table 3, was used instead of 2-(3-chloropropoxy)naphthalene(221 mg, 1.0 mmol), used in Example 18, the reaction was performed in the same manner as described in Example 18.

TABLE 3

	Alkyl halide or alkyl sulfonate	Reaction temperature(°C)	Reaction time(h)	Yield(%)
Ex.18		110	24	66
Ex.19		100	4	83
Ex.20		100	3	76
Ex.21		100	2	74
Ex.22		100	4	12
Ex.23		100	4	6
Ex.24		90	1.5	88
Ex.26		100	1.5	54
Ex.27		60	2	73
Ex.28		100	1.5	95

As the result shown in table 3, the yield of organic fluorocompounds varied according to alkyl halide or alkyl sulfonate that was being used, but it proved that if the reaction was accomplished for 1.5~4 hours at 60 ~ 110℃, the organic fluorocompounds can be obtained having an excellent yield.

INDUSTRIAL APPLICABILITY

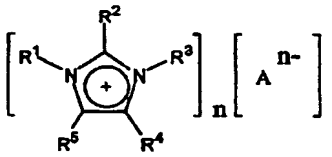
As explained hereinbefore, the present invention relates to a method for preparing organic fluorocompounds by reacting alkyl halide or alkyl sulfonate with fluoride salts in the presence of solvent, wherein the solvent is imidazolium salt with strong ionic character or a mixture solvent. When being reacted at a mild condition, organic fluorocompounds of a yield above 85% can be prepared. Organic fluorocompounds can be selectively prepared by increasing the solubility of fluoride salt using the above imidazolium salt, by increasing the displacement reaction rate using fluoride ion, and by inhibiting the side product caused by water.

The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method for preparing organic fluorocompounds by reacting alkyld halide or alkyl sulfonate with fluoride salts in the presence of solvent, wherein the solvent is imidazolium salt or a mixture solvent of imidazolium salts and organic solvent.

FORMULA 1



wherein, R^1 is $C_1 \sim C_{18}$ alkyl; R^2, R^3, R^4 and R^5 are hydrogen or $C_1 \sim C_{18}$ alkyl;

N is an integer of 1~3, and

A is an anion capable of forming salts.

2. The method according to claim 1, wherein R^1 is $C_1 \sim C_8$ alkyl; R^2 is hydrogen or $C_1 \sim C_6$ alkyl; R^3 is hydrogen or $C_1 \sim C_8$ alkyl, R^4 and R^5 are hydrogen or $C_1 \sim C_6$ alkyl.

3. The method according to claim 1, wherein R^1 is $C_1 \sim C_4$ alkyl; R^2 is hydrogen or methyl; R^3 is $C_2 \sim C_8$ alkyl; R^4 and R^5 are hydrogen.

4. The method according to claim 1, wherein imidazolium

salt of formula 1 is selected from a group consisting of 1-ethyl-3-methyl-imidazolium, 1-methyl-3-propyl-imidazolium, 1-butyl-3-methyl-imidazolium, 1-methyl-3-pentyl-imidazolium, 1-hexyl-3-methyl-imidazolium, 1-heptyl-3-methyl-imidazolium and 2,3-dimethyl-1-propyl-imidazolium.

5. The method according to claim 1, wherein the anion is MF_k^-, R^6O^-, $R^7R^8N^-$ or $R^9R^{10}R^{11}C^-$, wherein M is selected from a group consisting of 3~15 class elements in the periodic table, k is an integer of 2~6, R^6 is C_1~C_{12} alkylsulfone, halo C_1~C_{12} alkylsulfone, C_1~C_4 alkyl arylsulfone, halo arylsulfone, halosulfone, phosphoryl or perfluoro C_1~C_{12} alkylcarbonyl, R^7, R^8, R^9, R^{10} and R^{11} are all independent and can be C_1~C_{12} alkylsulfone, halo C_1~C_{12} alkylsulfone, C_1~C_4 alkyl arylsulfone, halo arylsulfone.

6. The method according to claim 1, wherein the anion of imidazolium salt of formula 1 is selected from a group consisting of PF_6^-, SbF_6^-, BF_4^-, NTf_2^- and TfO^-.

7. The method according to claim 1, wherein the imidazolium salt of formula 1 is 1-butyl-3methyl-methyl-imidazolium), and the anion is selected from a group consisting of BF_4^-, PF_6^-, SbF_6^-, NTf_2^- and TfO^-.

8. The method according to claim 1, wherein, the fluoride salt is potassium fluoride, the imidazolium salt being used is 1-butyl-3-methyl-imidazolium with an anion selected from a group consisting of BF_4^-, PF_6^-, SbF_6^-, NTf_2^- and TfO^-.

9. The method according to claim 1, wherein the content of imidazolium salt is 0.2 ~ 5.0 equivalents against alkyl halide or alkyl sulfonate.

10. The method according to claim 1, wherein the fluoride salt is alkali metal fluoride consisting of alkali metal selected from a group consisting of lithium, sodium, potassium, rubidium and cesium; alkaliearth metal fluoride consisting of alkaliearth metal selected from a group consisting of magnesium, calcium, strontium and barium; or ammonium fluoride.

11. The method according to claim 10, wherein the ammonium fluoride is selected from a group consisting of the forth ammonium fluoride such as tetrabutyl ammonium fluoride and benzyltrimethyl ammonium fluoride; the third ammonium fluoride such as triehtylammonium fluoride and tributylammonium fluoride; the secondary ammonium fluoride such as dibutylammonium fluoride and dihexylammonium fluoride; and the first ammonium fluoride such as

butylammonium fluordie and hexylammonium fluoride.

12. The method according to claim 1, wherein the fluoride salt is potassium fluoride.

13. The method according to claim 12, wherein the potassium fluoride is absorbed on the supporter selected from a group consisting of celite, molecular seive, alumina and silicagel.

14. The method according to claim 1, wherein the content of fluoride salt is 1.0~10 equivalents against alkyl halide or akyl sulfonate.

15. The method according to claim 1, wherein the organic solvent is selected from a group consisting of acetonitrile, tetrahdrofuran, 1,4-dioxane and t-butanol.

16. The method according to claim 15, wherein the organic solvent is acetonitrile.